Executive Summary of Year 3 Research Efforts

The primary goal of this three-year research program is to establish fusion bonding of semiconductor materials in an ultra-high vacuum (UHV) environment where the properties of the interface can be controlled with atomic-level precision. Such engineering of arbitrary hetero-interfaces can be utilized to enable new class of semiconductor optoelectronic devices. The UHV fusion bonding system was designed, constructed and improved in the first two years of the project. In the third year, a wide range of bonding processes has been attempted in UHV and nitrogen environments. More specifically, we (1) utilized the in-situ sputtering system to treat the semiconductor surfaces with selenium prior to bonding, (2) attempted argon and argon/hydrogen plasma treatment of the semiconductor surfaces prior to bonding, and (3) performed wet sulfur passivation techniques prior to introducing the samples into the UHV chamber. We have also arranged near-surface doping of our samples by ion implantation and UV laser annealing to induce surface dipoles. On the detector front, we improved the operational model for visible light photon counters and measured the timing jitter of the devices, which can be explained by the operational model.

Major Thrust and Accomplishments in the Third Program Year (March 2010-February 2011)

A. System Upgrades and Resulting Capabilities

As part of the third year effort, we continued to improve and add additional capabilities to the UHV fusion bonding chamber, focusing on the capability to pre-treat the surfaces prior to fusion bonding. At the end of Year 2, the only capability to treat the surface in-situ was thermal annealing. In the third year of the project, we added the following capabilities to the sputtering system that is connected to the UHV bonding chamber, to be able to treat the surfaces with various plasma and sputter-depositing thin layers of additional material. Furthermore, the primary surface characterization tool for our system was x-ray photoelectron spectroscopy (XPS): although XPS is a powerful tool to monitor surface composition, it cannot detect hydrogen, which does not have any core electron levels. We worked on the addition of ultraviolet photoelectron spectroscopy (UPS) capability to the system. Some highlights of the system installation and upgrades made in the third year include:

(1) Addition of DC/RF sputtering capability: The UHV fusion bonding system is connected to a sputtering chamber that has DC sputtering capability. However, the range of materials that could be deposited by the DC sputtering system is limited to metals. In order to sputter-deposit non-metal elements, we need an RF sputtering system. The DC sputtering guns that were installed in the system could easily be converted into RF sputtering guns if an RF power supply is provided, and the feedthroughs and grounds were adequately modified. We purchased an RF power supply (Seren R301 model, similar to the unit shown in Figure 1) and an impedance matching network to provide this capability, and was able to sputter elements like selenium onto the surface of the samples prior to bonding.

Figure 1: Seren R301 RF power supply.

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14. ABSTRACT
In this three-year research program, we designed and constructed a unique system capable of fusion bonding two wafers in an ultra-high vacuum environment. This system was integrated with a multi-chamber system that contains with XPS and UPS surface analysis tools and RF/DC sputtering system, to enable an experimental platform for insitu surface treatment, analysis, and bonding. We have developed various methods for preparing oxide-free silicon surfaces in UHV environment, and attempted in-situ fusion bonding of silicon wafer and InGaAs wafer. We have successfully demonstrated fusion bonding between HF-dipped silicon wafer and InGaAs wafer in UHV environment. On the device side, we have developed a detailed operational model of the VLPC devices. The device modeling capability provides us with the possibility of designing new generation of VLPC devices that feature improved performance characteristics, such as reduced timing jitter, high efficiency in the UV and telecommunication wavelength range, and lower dark counts.

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(2) Addition of plasma treatment capability: When the RF bias is applied to the sample holder in the presence of gas such as Ar, an RF plasma is created and the sample surface can be treated with plasma. The sample holder in the sputtering chamber was grounded for DC sputtering in our system, so we had to make modifications on the sample chuck to electrically isolate it from the rest of the chamber. We designed and machined an isolator with MACOR, and added an RF feedthrough to the sputtering chamber to enable plasma treatment of the samples. The same RF power supply and matching network could be used to strike RF plasma by biasing the sample chuck. We also added additional mass-flow controllers to the system to introduce controlled amount of argon and argon/hydrogen mixture as the plasma treatment environment. A fine control for the gate valve between the chamber and the turbo pump was added to enable the control of the plasma treatment environment.

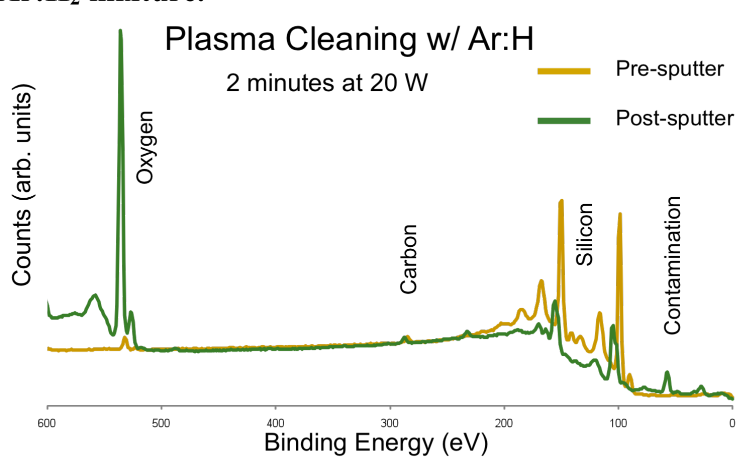
(3) Ultraviolet Photoelectron Spectroscopy (UPS) capability: The current system is equipped with a used UPS system from SPECS that we inherited from a lab in RTI International, which was not operational. We dedicated quite a bit of time in the third year in an attempt to fix this equipment so that we can measure the surface concentration of hydrogen, which cannot be monitored using the XPS system. The UPS system operates by creating a plasma of He gas in the gun, and propagating the generated UV radiation through a capillary tube towards the sample area. In order to create the He plasma, the pressure inside the gun should be maintained at millitorr pressures while the sample/analysis chamber must be maintained below 10^{-9} Torr pressure range. We also discovered that the capillary tube that guides the UV radiation is contaminated and was too short to deliver the UV radiation all the way to the sample. In our attempt to revive the system, we added a small turbomolecular pump and a dry scroll backing pump to maintain the high differential pressure between the UV gun and the sample/analysis chamber. We also replaced the capillary tube and extended its length to the sample area. Despite these efforts, we were not able to bring the UPS up to an operating condition mainly due to the lack of experience in operating such a system. At this time, the UPS system remains non-operational, and we were not able to utilize this tool for the surface characterization of our samples.

B. Wafer Bonding Process Development in UHV Environment

With the additional capabilities enabled by these upgrades, we have attempted several different variations of the fusion bonding attempt in the UHV environment. In addition, we have also developed a few other pre-treatment techniques based on surface preparation results reported in the literature. We summarize our attempts and the bonding results here.

(1) Plasma cleaning of samples for removing hydrogen: The first experimental effort was to try to treat the silicon sample surface with Ar plasma for a short period of time to remove the hydrogen adsorbed on the surface. The initial plasma treatment

Figure 2: XPS scan of the silicon surface treated with Ar:H_2 mixture.

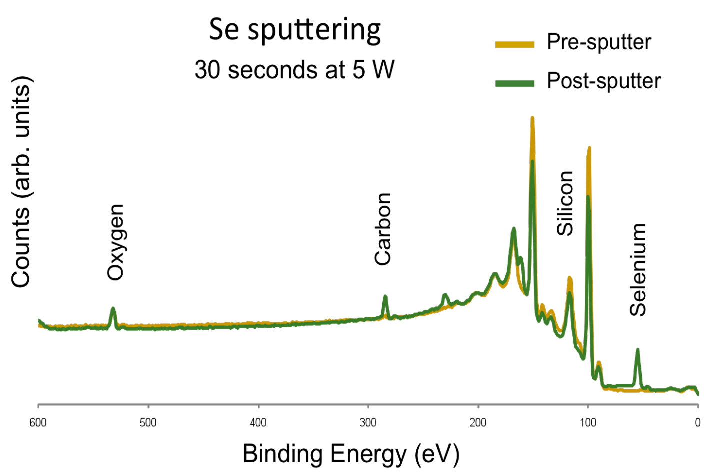


showed elevated levels of oxygen contamination, which is an undesirable effect. We introduced a mixture of Ar and hydrogen into the treatment mixture, in an attempt to create reducing environment to slow down the oxidation. Figure 2 shows the XPS scan of the silicon surface treated with Ar:H_2 plasma. Yellow trace shows the pre-treatment surface with low levels of oxygen and strong silicon peaks, while the post-treatment surface develops large oxygen peaks, and silicon peaks shift demonstrating oxide contamination.

In addition to the contaminated surface, the bonding experiments in the UHV bonding chamber has been unsuccessful despite multiple bonding attempts.

(2) Selenium sputtering on silicon surface for fusion bonding: Removal of hydrogen from silicon surface leaves active dangling bonds, which is known to reconstruct the surface to a stable configuration by forming strong covalent bonds with each other. Hydrogen is known to terminate these dangling bonds while avoiding reconstruction, leading to 1x1 reconstruction surfaces on silicon [100] surface. We found in the literature that group VI elements such as sulfur and selenium could lead to 1x1 silicon surface also avoiding reconstruction. We attempted sputtering selenium onto silicon surface after treating the silicon in HF. The silicon surface was cleaned and dipped in HF, which provides hydrogen-terminated surface. Then, it was loaded into the UHV chamber and moved to the sputtering system. A thin layer of selenium was deposited onto the silicon surface by the sputtering a pure selenium target. The surface was carefully studied using XPS for the presence of selenium and other potential contaminants. Figure 3 shows the XPS spectrum of the silicon surface treated with selenium sputtering for 30 seconds at very low RF power. We can clearly see selenium peak, as well as a small carbon peak that appears after selenium sputtering. Prolonged sputtering or sputtering at higher RF power levels lead to severe oxidation of the silicon surface, similar to that seen under Ar or Ar:H_2 plasma treatment as shown in Figure 2.

Figure 3: XPS scan of silicon surface treated with selenium sputtering.



The bonding experiments with selenium treated silicon surfaces have also been unsuccessful despite many bonding attempts.

The sputtering and plasma treatment experiments showed significant levels of oxygen contamination upon prolonged exposure to RF plasma. We attribute this to (1) poor vacuum condition in the sputtering chamber (>10^{-7} Torr) compared to other parts of the UHV system (≤10^{-9} Torr), (2) aluminum construction of the main chamber instead of stainless steel, and (3) the pumping system for the sputtering chamber, which consists of a turbomolecular pump backed by an oil-based mechanical pump. While these conditions might be adequate for conventional sputtering tools, we suspect it has too much uncontrolled contaminants that is actively liberated from the internal surfaces of the chamber when a plasma is ignited leading to contamination.

(3) It is known that sulfur can replace oxygen on the surfaces of semiconductors, leading to passivated surfaces in III-V compound semiconductors. Sulfur forms shallow donor impurity states in most III-V semiconductors instead of deep mid-gap impurity levels oxygen impurities create. Such oxygen defects act as an efficient non-radiative recombination center near the surface, leading to performance degradation in most optoelectronic devices. Sulfur passivation techniques were developed to replace the deep oxygen impurities with shallow sulfur impurities improving the performance of light emitting devices in III-V compound semiconductors. In these sulfur passivation techniques, the samples are typically dipped in sulfur-containing solutions such as $(NH_4)_2S$, and then the surface is encapsulated in inert films such as silicon nitride to avoid further oxidation of the surface.

We attempted sulfur passivation of the silicon and InGaAs surface prior to bonding. The sulfur passivation was performed by dipping either or both of silicon and InGaAs samples into $(NH_4)_2S$ solution after the surface cleaning process. The samples are then bonded in air and then annealed in a high temperature (~650°C) environment to induce fusion. We have observed successful bonding of these sulfur-passivated surfaces, and the valence band discontinuity was measured across the junction. We concluded that the measurement results did not significantly deviate from the hydrogen-terminated surfaces. Furthermore, the bonding yield was very low, and the carrier transport across the junction seems to be hindered by the presence of oxide barriers at the junction.

(4) Summary of bonding results: Between Year 2 and Year 3 of this project, we have attempted many wafer bonding experiments with a wide range of surface treatment conditions. Table 1 summarizes the results of the bonding attempts. The only successful bonding attempt in UHV environment involves hydrogen termination of the bonding surfaces. Other successful bonding experiments failed to produce substantial discontinuity in the valence band to date. Careful inspection of samples surfaces on failed bonding attempts seem to indicate that the silicon surface is very stable and fails to make covalent bond with the InGaAs surface, prohibiting the formation of a strong fusion-bonded interface. We have not yet successfully identified the surface treatment condition under which the silicon and InGaAs surface will bond with high yield and with high transparency (*i.e.*, no oxide barriers), but features significant deviation of the valence band discontinuity. We lacked the analysis tools to study the presence of hydrogen atoms or the surface reconstruction status of the silicon after various treatment methods, and can only suspect that the role of hydrogen in enabling high yield bonding is critical.

Table 1: Summary of wafer bonding attempts and results.

Bonding Environment	Si Surface Treatment	InGaAs Surface Treatment	Bonding Success	Valence Band Discontinuity	Remarks
N_2 (Air)	HF Dip	HF Dip	O	0.41-0.56eV	Control sample
UHV	HF Dip	HF Dip	O	0.61eV	Need more statistics
Air	HF/$(NH_4)_2S$ Dip	$(NH_4)_2S$ Dip	O	0.58eV	Oxide barrier, poor yield
Air	HF Dip	$(NH_4)_2S$ Dip	O	0.54eV	Oxide barrier, poor yield
UHV	HF/Thermal	HF	×		Sample cracking
UHV	HF/Se	HF	×		Sample cracking
UHV	HF/Thermal/Se	HF	×		Sample cracking
UHV	HF/Ar:H Plasma	HF	×		Si surface contaminated

(5) Future research directions: We plan to continue to explore other methods of modifying the band alignment, using shallow surface doping prior to fusion bonding. For this purpose, we have grown some InGaAs layers with a delta-doped layer (silicon dopants), and some silicon wafers with very shallow ion implantation. The implanted silicon wafers are annealed using a UV laser, which is known to only heat up the surface and activate the dopants very close to the surface. When bonded, these layers are expected to form a dipole layer at the interface, creating a shift in band alignment compared to conventional material. We have successfully prepared the material sets, but did not quite get an opportunity to try to bonding with these materials in time to be included in this report. Exploring these effects will be the subject of future research in this area.

C. Improved physical model and timing jitter of Visible Light Photon Counters

(1) In the final year of this project, we worked on improving the physical model for the VLPC detectors to understand the gain, dark counts, quantum efficiency and timing jitter characteristics of the device. In a recent paper we published [1], we presented a detailed carrier transport and gain model for the VLPC detectors. We analyzed the carrier generation process for a VLPC device assisted by the Poole-Frenkel effect, and the gain experienced by these thermally generated carriers based on an impact ionization model of the donor impurities by minority electrons in the conduction band saturated by space-charge effect. Based on these two models, we developed a self-consistent method to calculate the electric field profile of the VLPC devices under normal operating conditions, as shown in Figure 4. The electric field profile estimated this way allows us to extract various operating parameters of the device including quantum efficiency, dark counts, gain and its variation, and timing jitter.

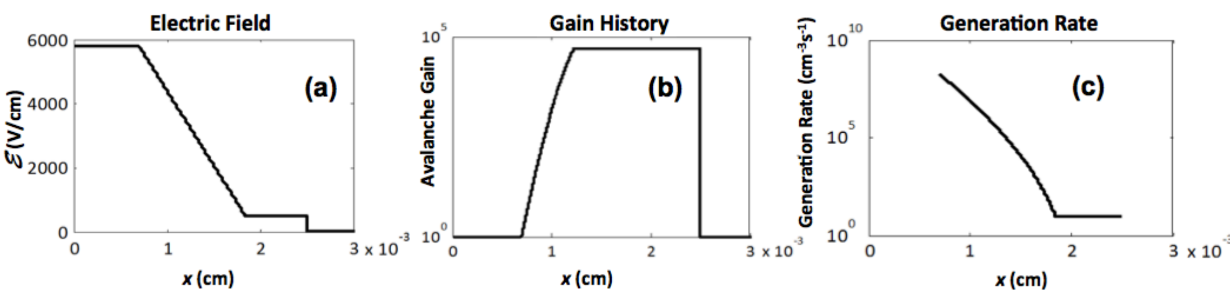


Figure 4: Calculated electric field, gain and thermal generation rate of VLPC devices based on the self-consistent method developed under this project.

The developed model provides a path to improving critical performance metrics of VLPCs as a high quality single photon detector. In the paper, we proposed (1) a waveguide photon detector that extends VLPC operating wavelength range to telecom wavelength (shown in Figure 5), which is consistent with the main device-level objective of this project, (2) reduced dark count detectors by reducing the thermal generation rate and overall device area, and (3) low timing jitter devices by reducing the thickness of the layers over which the electrons move with low drift velocity.

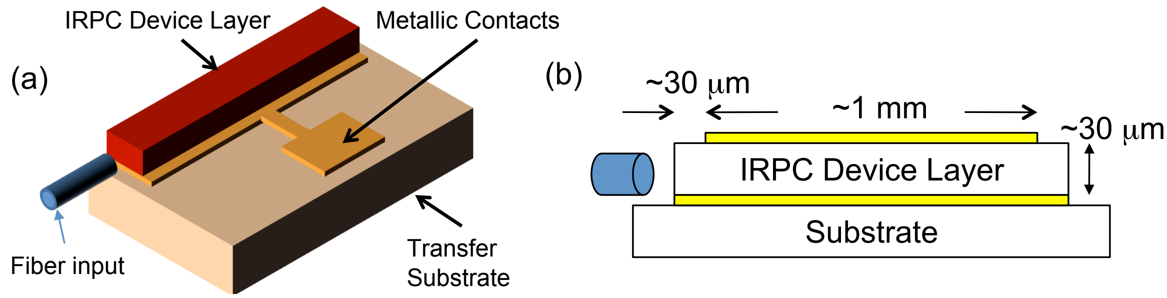


Figure 5: Waveguide single photon detectors based on VLPC operating principles. Edge-illumination geometry allows one to achieve very high quantum efficiency single photon detection in the telecommunication wavelength band, which is consistent with the main device-level objective of this project.

(2) Timing Jitter Measurement for VLPCs: In collaboration with the photonic device group at NIST in Boulder, CO, we published a paper on the timing jitter characteristics of the VLPC at different wavelengths, bias voltages, and temperature [2]. Figure 6 shows the experimental configuration (left) of the timing jitter measurement, where the output of an ultrafast Ti:Sapp laser pumps a photonic crystal fiber to generate supercontinuum. The output of the supercontinuum is filtered through a grating monochromator (GM) so that a short pulse of photons over a wide wavelength range can be selectively injected onto the VLPCs. The output signal from the VLPC is correlated with the arrival time of the pump laser pulse to provide the timing jitter information for the VLPC device. The figures in the middle and on the right shows the timing jitter measured as a function of device bias voltage and the incident photon wavelength. The dependence of the timing jitter on wavelength and bias voltages, when interpreted through the carrier dynamics model described in the previous section, indicates that the primary source of timing jitter in VLPCs is the drift of secondary electron through the drift region where it moves with low mobility/drift velocity. Modifying the electric field profile under operating conditions to reduce the drift layer thickness or increase the drift velocity there could lead to improved timing jitter performance.

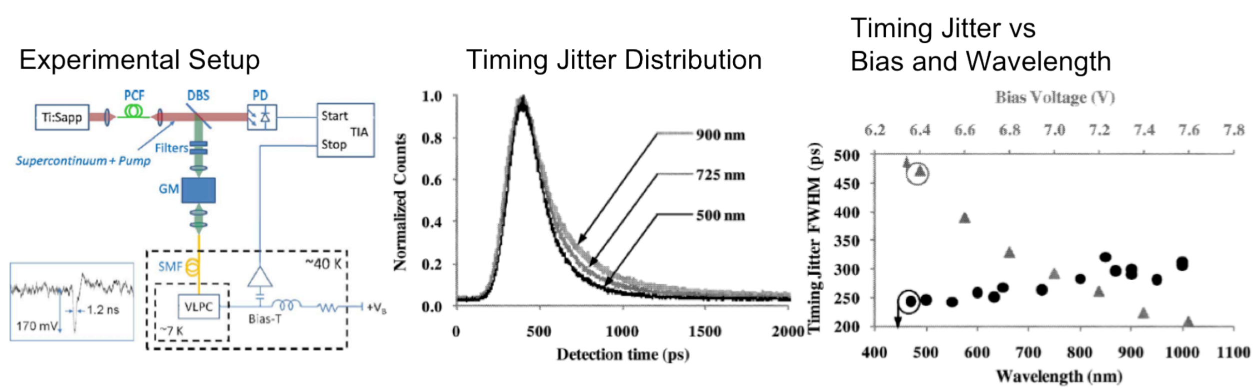


Figure 6: Experimental configuration (left), timing jitter distribution as a function of input photon wavelength (center) and the FWHM timing jitter as a function of device bias voltage and incident photon wavelength (right) for VLPCs.

Overall Achievement of the Project

Through the three-year research program, we have achieved the following progress in the field:

1. **Design and Construction of UHV Wafer Bonding System**: Major effort in the research program was dedicated to establishing a wafer fusion bonding system under UHV conditions. This system was integrated with an existing multi-chamber system with XPS and UPS surface analysis tools and DC sputtering system. We have added RF sputtering and plasma treatment capabilities to this system to enable an experimental platform for in-situ surface treatment, analysis, and bonding. The details of the design and construction of this system have been documented in our manuscript, which will be submitted for publication shortly [3].
2. **Development of Oxide-free Silicon Surfaces in UHV Environment**: We have developed various methods for preparing oxide-free silicon surfaces in UHV environment. The methods we have tested includes (1) HF dip in air followed by thermal anneal in UHV, (2) RCA clean to grow thin oxide, followed by thermal anneal in UHV, and (3) HF dip in air followed by short selenium sputtering in vacuum. We have successfully demonstrated fusion bonding between HF-dipped silicon wafer and InGaAs wafer in UHV environment, but none of the other UHV-prepared surfaces featured successful bonding. The role of hydrogen in the bonding process requires further studies in the future.
3. **Characterization and Operational Models of VLPC Detectors**: We have developed a detailed operational model of the VLPC devices. Based on this model, we could explain the timing jitter characteristics of the VLPCs observed experimentally. Furthermore, the device modeling capability provides us with the possibility of designing new generation of VLPC devices that feature improved performance characteristics, such as reduced timing jitter, high efficiency in the UV and telecommunication wavelength range, and lower dark counts.

References / Publications

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